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ELECTROCHEMICAL PROCESS FOR THE MANUFACTURING OF TITANIUM ALLOY MATRIX COMPOSITES

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The paper presents a new method for precursors' synthesis of titanium alloys matrix composites through an electrochemical process in molten calcium chloride. The cathode of the cell was made from metallic oxides powders and reinforcement ceramic particles, which were pressed and sintered into disk form and the anode from graphite.
The process occurred at 850 °C, in two stages, at 2,7 / 3,2 V: the ionization of the oxygen in oxides and the reduction with calcium formed by electrolysis of calcium oxide fed in the electrolyte. The obtained composite precursors, in a form of metallic sponge, were consolidated by pressing and sintering. Chemical and structural analyses on composites samples were performed.

Key words: titanium, composite, oxides, electrochemical reduction

Elektrokemijski postupak za proizvodnju titanovih kompozitnih slitina. Članak prikazuje novu metodu prethodne sinteze titanovih kompozitnih slitina s elektrokemijskim postupkom u rastaljenom kalcijevom kloridu. Katoda ćelije ustrojena je od praškastog metalnog oksida ojačan keramičkim česticama, koji je stlačen u obliku diska, a anoda je od grafita.
Postupak se odvijao na 850 °C u dva stupnja, 2,7/3,2 V: ionizacija kisika u oksidima i redukcija kalcijem nastajala je elektrolizom kalcijevih oksida u elektrolitu. Dobiveni prethodno kompozit u obliku metalne spužve je očvrsnut tlačenjem i sinteriranjem. Provedena je kemijska i strukturna analiza uzoraka kompozita.

Ključne riječi: titan; kompozit; oksid; elektrokemijska redukcija

INTRODUCTION

Titanium matrix composites (TMC) represent a perspective materials category with potential applications in many important fields like aerospace constructions, automotive industry, ship structures, sports and households objects, and others.

A titanium matrix composite is constituted of a titanium or titanium alloy – matrix and reinforcements materials, which are usually ceramics in form of particles or fibres [1]. Titanium matrix composites combine the good mechanical characteristics as strength, ductility, toughness, and the damage tolerance of titanium alloys with the high strength, stiffness and creep resistance of ceramic reinforcements (i.e. silicon carbide, titanium boride, titanium carbide, etc.).

A reduction of the composites' density toward the matrix alloy is owed to reinforcements.

Titanium alloys used as matrixes in TMC are of different types, chosen for their specific high properties: high mechanical tensile and fatigue strength, raised Young modulus, or good heat resistance. So, several current alloys used as matrix are: TiAl6V4, TiAl5Sn2,5, TiAl8Mo1V1,0, TiFe4,3Mo7,0Al1,4V1,4, etc.

The suitable reinforcements for TMC related as being used or investigated in scientific studies, are: silicon carbide coated boron as continuous fibers; titanium diboride, titanium carbide, silicon carbide, aluminium oxide and other ceramic particles. The reinforcements in TMC extend titanium operating temperature range from 300 °C ÷ 400 °C up to 600 °C. The main applications of TMC are in aeronautical constructions as structural materials and as components for engines, landing gears, etc. These high performance materials tend to be used in automotive constructions such as automobile engines, drive train components or general machine components. There are several fabrication methods of TMC which are presented in known processes and patents.

Current obtaining methods can be divided into two major categories [2]. Primary fabrication methods are used to create the TMC from its constituents. The resulting material may be in a form close to the final configuration, or it may require considerable additional processing, called secondary fabrication, such as forming, rolling, metallurgical bonding and machining. The used

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processes depend on the type and form of reinforcement and matrix.

The most used or investigated methods for TMC obtaining are: solid state processing by powder metallurgy processing for particulate TMC or by components pressing, extrusion, rolling at high temperatures; liquid state processing by the forced infiltration of a liquid matrix through a fiber pre-form or thermal / plasma spraying of metallic matrixes on prearranged fibers; vapor state processing by different fibers coating methods. The actual methods for TMC obtaining confront with several difficulties such as: large number of technological operations for reinforcement treatments and composite consolidation; difficult machining; high processing costs, which are added to the raised price of the titanium alloys semi-finished components and of the coated reinforcements.

Due to these considerations, despite their excellent characteristics, the area of applications for TMC is very limited to domains which can support the high production costs.

The present work proposes a new method to obtain high performance as well as low cost titanium alloy MMC, using recent developments in titanium and other metallic materials by an electrochemical process developed in molten salts [3-7].

The method was experimented for obtaining the precursors of metal matrix composite Ti-Al6-V4 titanium alloy / $TiB_{2\ particles}$. This method consists in the reduction of Ti, Al and V oxides' mixture in which the ceramic reinforcement particles were initially introduced, through an electro - de-oxidation/reduction process using molten calcium chloride as electrolyte. TMC precursors obtained in a pre-sintered powder sponge form were further thermally – mechanically processed for final composite consolidation.

EXPERIMENTAL RESEARCHES

As composite's matrix was established the most known Ti-Al6-V4 alloy, having an alpha-beta structure with high mechanical tensile and fatigue strength. The introduced reinforcement material -TiB_2 particles- is very stable and don't request additional coatings to achieve a strong bonding with the matrix alloy [6].

In the first stage of the experimental works, cathodes were manufactured with powder blending, pressing and sintering of the oxides – boride mixture.

The cathodes of the electrolysis cell are disks with the dimensions 30 mm diameter and 5 mm height, jointed in a metallic holder. The constitutive powders' mixture contained Ti, Al and V oxides, of weight in accordance with the alloy's chemical composition, and a fraction of 10 % weight TiB_2. The weight doses from oxide / reinforcements mixture, for each cathode, were pressed in a die with a force of ~ 60 kN.

Table 1. **Cathodes' raw materials**

Material	Purity / %	Particles dimensions / μm
Titanium oxide TiO_2	99,9	~ 5
0Aluminum oxide Al_2O_3	99,7	< 10
Vanadium oxide V_2O_5	p.a.	~ 10
Titanium diboride TiB_2	p.a.	~ 10
Calcium chloride $CaCl_2$	p.a.	100 – 500

Table 2. **Characteristics of the cathode disks**

Materials	Cathode pressed disks				
	G / g	*d* / mm	*h* / mm	*C* / %	*P* / %
TiO_2, Al_2O_3, V_2O_5, TiB_2	7,52	30	5,52	46,06	53,94
	7,53	30	5,56	45,79	54,21
Materials	**Cathode pressed – sintered disks**				
	G / g	*d* / mm	*h* / mm	*C* / %	*P* / %
TiO_2, Al_2O_3, V_2O_5, TiB_2	7,46	28,2	5,39	52,96	47,04
	7,45	28,2	5,44	52,41	47,59

Note: *G* – weight; *d* – diameter; *h* – height
C – compacted fraction; *P* – porosity.

The pressed disks were sintered for 3 hours at 650 ^{0}C under controlled atmosphere (Ar). The main characteristics of the oxide mixture disk after the pressing and sintering processes are presented in Table 2.

The experimental installation for titanium alloys obtaining is presented in Figure 1.

The main components of the installation are: a special designed electrochemical reduction cell of approx. 0,5 liters volume, from silicon and aluminum oxynitride which was introduced in an electrical furnace, a current power supply through a potentiostat and a device for purification and feeding of the inert gas.

The electrochemical process was carried out at 850 °C in two stages, Figure 2.

In the first stage, the cell voltage was $U = 2,7$ V (below the decomposition potential of CaO). The duration of the first stage was approx. 400 min; during this period the current continuously decreased from approx. $I = 3,2$ A, to a constant value of approx. 0,2 A.

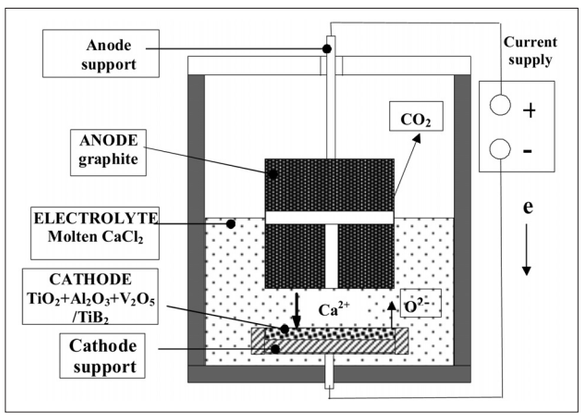


Figure 1. The draft of the electrolysis cell

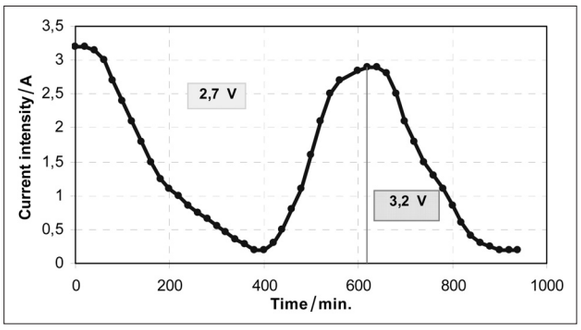


Figure 2. Current variation during the electrochemical reduction process of the $TiO_2 - Al_2O_3 - V_2O_5$ / TiB_2 cathodic mixture.

In the second stage the quantity of ~ 7 % weight CaO was added, and the voltage was increased up to U = 3 V (below the decomposition potential of $CaCl_2$). In this stage, the value of current sharply raised to $I \sim 3$ A. Then, the current value dropped in approx. 200 min. to 0,3 ÷ 0,2 A; for still 150 min., this value was maintained almost constant.

The total duration of the entire process was approx. 15 hours. At the end of the process, the electrolyte was siphoned into a preheated metallic crucible. After cooling, the cathode disk was drawn out and washed with 0,1N HCl solution, at 75 °C, for the removal of impregnated $CaCl_2$. The cathode disk, in a sponge form, made of quasi-metallic alloy with Ti, Al and V particles, and TiB_2 integrated particles represent a composite's precursor.

Composite precursors were processed by powder metallurgy methods (pressing and sintering) in order to obtain Ti-Al6-V4 alloy / TiB_2 composite samples.

The pressing operation was performed in a cylindrical shape die, in which two composite precursor's disks with the same composition, having approx. 28 mm diameter and 5 mm height dimensions were charged. A pressing force of almost 250 kN value was applied.

The titanium alloy matrix composite was achieved by sintering in argon atmosphere at 1150 °C and the duration of about 5 hours.

The weight and the dimensional features of two Ti-Al6-V4 / $TiB_{2\ particles}$ composite disks are presented in Table 3.

Table 3. **Composite weight and dimensions**

Composite precursor	*G* / g	*d* / mm	*h* / mm	ρ / g/cm^3	*C* / %	*P* / %
Sample 1	14,9	29,9	5,47	3,88	88,3	11,7
Sample 2	14,8	29,9	5,42	3,89	88,6	11,4
Composite pressed-sintered	*G* / g	*d* / mm	*h* / mm	ρ / g/cm^3	*C* / %	*P* / %
Sample 1	14,7	29,5	5,32	4,04	92,1	7,9
Sample 2	14,6	29,5	5,27	4,06	92,3	7,7

Note: *G* – weight; *d* – diameter; *h* – height
C – compacted fraction; *P* – porosity.

RESULTS AND DISCUSSION

The experimental samples obtained in different stages were characterized with: chemical analysis of the reduced cathode; chemical analysis of the electrolyte; structural electronic microscopy and diffraction analyses of composites precursors; structural optical microscopy analyses of Ti-Al6-V4 alloy/$TiB_{2particles}$ composite samples.

Chemical compositions of two reduced cathodes' samples are presented in Table 4.

Table 4. **Reduced cathodes' compositions**

Sample	Chemical composition / weight %						
	Al	V	O_2	Ca	Cl	B	Ti
I	5,37	3,55	0,18	0,03	0,02	3,22	Bal.
II	5,46	3,52	0,24	0,02	0,09	3,15	Bal.

Calculated as a function of boron contents, the contents of the reinforcement in the composites samples are of 10,4 % weight (9,6 % vol.), respectively 10,1 % weight (9,4 % vol.) TiB_2.

The alloy's composition is situated within the standard limits for Al and V contents.

The residual oxygen content is generally in the allowed limits of the Ti alloy. The small calcium and chlorine contents came from residual electrolyte.

The electrolyte chemical composition is given in Table 5.

Table 5. **Chemical composition of the electrolyte**

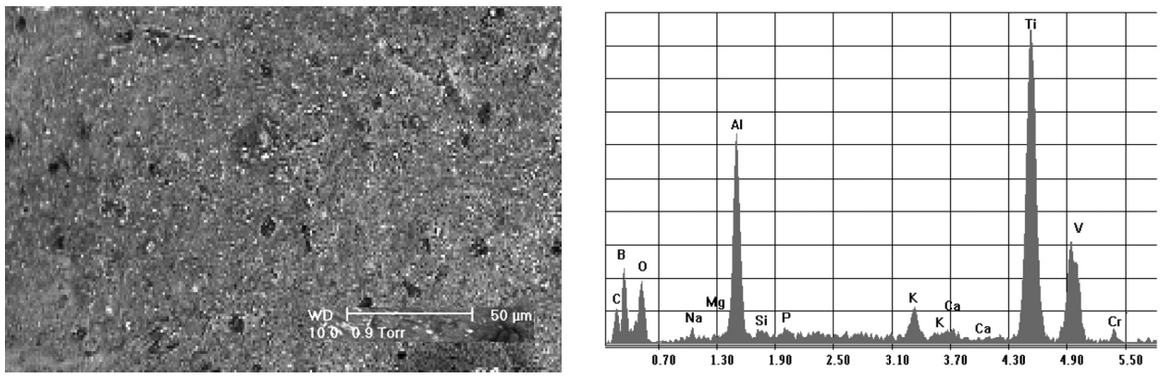
Electrolyte composition	weight %			
	Ca	Cl	O	Fe
Before CaO feeding	35,89	Bal.	0,58	0,05
Sample – after electrolysis	38,42	Bal.	2,12	0,03

The higher content of oxygen and calcium in the electrolyte sample after electrolysis is due to the CaO introduced and reformed as a result of the Ti, Al, V oxides reduction with cathodically deposited Ca.

SEM electronic microscopy of reduced cathode (composite's precursor) after washing and drying reveals a homogeneous and porous structure (Figure 3.a). Black pores with 5 ÷ 10 μm in size and 6 – 8 % total surface can be distinguished.

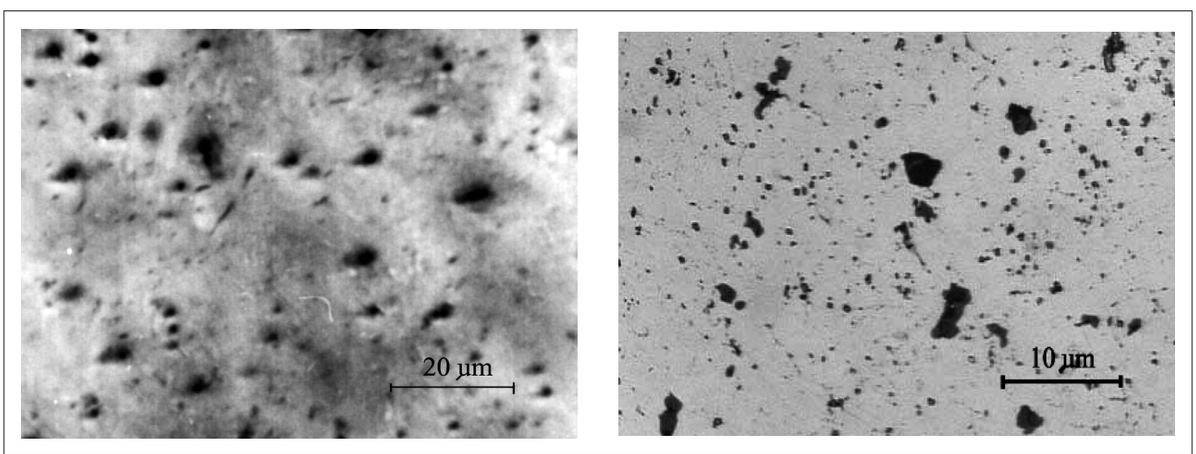
The main constituents in the Ti-Al6-V4/TiB_2 composite structure are: the titanium alloy partially homogenized with diffusion, which keeps yet a granular aspect; a quantity of approx. 10 % TiB_2 compounds having light – grey colors.

The composition of a composite's precursor sample, determined with an electronic microscope of XL – 30 – ESEM TMP and EDAX analyzer type shows the main constitutive elements of the alloy's matrix and of the inserted compounds, respectively Ti, Al, and B. The



a. **b.**

Figure 3. Microstructure and composition of a Ti-Al -V/ TiB_2 precursor composite (electrolyzed cathode) determined by SEM and EDAX analyses.



a. **b.**

Figure 4. The Ti-Al6-V4 alloy / $TiB_{2\ particles}$ composite's structure by optical microscopy

height of the peaks gives a semi-quantitative estimation on the elements' composition.

Structural optical microscopy analyses of Ti-Al6-V4 /$TiB_{2\ particles}$ composite's samples, obtained from cathode precursors with pressing and sintering with an additional diffusion heat treatment.

On the microphotographs (Figure 4) black pores of irregular shape, up to 10 µm size, and also, grey-dark smaller compounds which are uniformly distributed in the titanium alloy matrix are found. The alloy matrix, the main constituent of the structure, is homogeneous at the used magnifications.

The interfaces between the reinforcement particles and the matrix, observed at higher magnifications, are very tight. There are necessary supplementary investigations to reveal the matrix-particles junction and possible intermediate layers.

The titanium matrix alloy obtaining with oxides electrochemical reduction accompanied by solid state diffusion has the advantage of a raised chemical reactivity. Furthermore, the "in situ" composite's precursor obtaining is favored by the matrix-reinforcement binding between active surfaces.

The uniform distribution of the reinforcing particles can be assured from the early stages of the process, by blending conditions and the established particles sizes of the cathode component powders.

The temperature of electrolytic reduction process during the composite's precursor synthesis is significantly lower than in the case of titanium matrix composites obtaining by the known liquid state procedures.

On the other hand, this temperature allows the development of a diffusion process for titanium alloy's matrix forming and for the matrix-reinforcement particles embodying.

In comparison with the classical procedures for the metal matrix composites obtaining, by the proposed method for the composite's precursor forming a small number of operations is necessary.

An important advantage of the new method is the use of oxides as raw materials instead of metals; these up 10 times chipper materials have a great influence on the composite final costs.

The reinforcing elements can be used without any supplementary coating treatments which are achieved by special, difficult and expensive operations.

The specific energy consumption of the electrolysis is low, since the process occurs at very small potentials ($U \sim 3$ V) and moderate current densities.

CONCLUSIONS

The performed experiments proved that the TMC synthesis using the electrochemical reduction of the oxides is feasible.

A preliminary assessment of the experimental works and of the results reveals that the new method has a significant potential for matrix composites obtaining. Titanium and other high fusible and reactive metals matrixes are suitable for the process.

In order to become a real technological alternative, new research works must be achieved to elucidate the kinetics of the chemical reactions which take place in the complex system, the forming mechanism of the reinforcement-alloy matrix bonding, as well as the physical-chemical processes which occur at the pressing-sintering of the composite precursor cathodes.

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Note: V. Soare is responsible for the English language.